" Preliminary Note on a Method of Calculating Solubilities, and the Equilibrium Constants of Chemical Reactions, and on a Formula for the Latent Heats of Vaporisation." By ALEXANDER FINDLAY, M.A., B.Sc., Ph.D. Communicated by Professor RAMSAY, F.R.S. Received February 1,—Read February 13, 1902.

I. A number of years ago, it was shown by Ramsay and Young,[*] that for any pair of closely related substances, the ratio of the absolute temperatures corresponding to equal vapour pressures is constant, *i.e.*, $T_1/T'_1 = T_2/T'_2$. In the case of substances not closely related, it was shown, generally, that the relation between the absolute temperatures at which the two substances have equal vapour pressures could, with very great approximation, be expressed by the equation, $R = R' + c(t' - t)$, R being the ratio of the absolute temperatures, $T/T'$ or $T'/T$, at which the substances both have any given vapour pressure; $c$ is a constant which may be 0 or a small positive or negative number; and $t'$ and $t$ are the temperatures of one of the substances corresponding to these two vapour pressures. Or, since the variation of the ratio R from constancy was found to be practically a linear function of the temperature, we may also express the above relationship by means of the equation $T/T' = a + bT$. In this equation $a$ is of the order unity, and $b$ of the order 0·001 to 0·0001, and $-b$ is equal to $+c$ of the previous equation. It was further shown by Ramsay and Young that by means of the above equation, if the vapour pressure curve of one substance is known, the vapour pressure curve of any other substance can be calculated from the values, at any two temperatures, of the vapour pressure of that substance. The above relationship was tested by Ramsay and Young in the case of 23 pairs of substances, and has also been found to hold up to the critical pressure.[†]

The degree of success with which the method can be used, is shown by Table I, which I take from the memoir of Ramsay and Young above mentioned.

At the suggestion of Professor Ramsay, I undertook the investigation of whether any similar method could be obtained for the calculation of solubilities; and I have found that a precisely similar equation to that of Ramsay and Young connects the absolute temperatures at which two substances have equal solubilities; that, therefore, the equation $R = R' + c(t' - t)$ holds good with respect to the *solubilities* of any two substances. In this equation R and R' now denote the ratios of the absolute temperatures at which the substances have equal solubili-

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[*] 'Phil. Mag.,' 1886, vol. 21, p. 33.

[†] In this way the vapour pressures of argon, krypton, and xenon have been calculated by Ramsay and Travers ('Phil. Trans.,' A, vol. 197, 1901, p. 47).

Table I.—Calculation of the Vapour Pressures of Carbon Disulphide
from the Vapour Pressures of Water.

$$c = 0\!\cdot\!0006568.$$

| Pressures in mm. | Abs. temps. of water. | Ratios of abs. temps. of $CS_2$ to those of $H_2O$. | Smoothed ratios. | Re-calculated abs. temps. of $CS_2$. | Observed abs. temps. of $CS_2$. |
|---|---|---|---|---|---|
| 50   | 311·3   | 0·8161 | 0·8160 | 254·0  | 254·05 |
| 100  | 324·7   | 0·8245 | 0·8242 | 267·6  | 267·7  |
| 150  | 333·1   | 0·8301 | 0·8296 | ·276·3 | 276·5  |
| 200  | 339·6   | 0·8339 | 0·8338 | 283·2  | 283·2  |
| 300  | 348·9   | 0·8403 | 0·8400 | 293·1  | 293·2  |
| 400  | 356·0   | 0·8448 | 0·8449 | 300·8  | 300·75 |
| 500  | 361·7   | 0·8485 | 0·8483 | 306·8  | 306·9  |
| 600  | 366·5   | 0·8517 | 0·8519 | 312·2  | 312·15 |
| 700  | 370·7   | 0·8545 | 0·8545 | 316·8  | 316·75 |
| 800  | 374·45  | 0·8567 | 0·8571 | 320·9  | 320·8  |
| 900  | 377·8   | 0·8589 | 0·8590 | 324·5  | 324·5  |
| 1000 | 380·85  | 0·8612 | 0·8611 | 327·95 | 328·0  |
| 1500 | 393·2   | 0·8695 | 0·8692 | 341·8  | 341·9  |
| 2000 | 402·5   | 0·8753 | 0·8757 | 352·5  | 352·3  |
| 3000 | 416·5   | 0·8852 | 0·8850 | 368·6  | 368·7  |
| 5000 | 435·85  | 0·8987 | 0·8978 | 391·3  | 391·7  |

ties; $c$ is a constant which may, possibly, have the value 0, but which,
in all the cases I have examined, has a small positive or negative value;
$t'$ and $t$ are the temperatures at which one of the substances has the
two values of the solubility in question. *The above equation also holds
no matter whether the substances are ionised or are non-ionised, or whether
their heat of solution is positive or negative.*

A method, which is in all points analogous to that employed by
Ramsay and Young* for the calculation of vapour pressures, can thus
be made use of for the calculation of solubilities. In order to calcu-
late the solubility of any substance B by means of the known values
of the solubility of another substance A, one proceeds as follows:—
The solubility of B at any two absolute temperatures $T'_1$ and $T'_2$
is determined. On dividing these temperatures into the tempera-
tures $T_1$ and $T_2$, at which A has the same solubility, the ratios
$T_1/T'_1$ and $T_2/T'_2$ are obtained. These ratios are now plotted as
abscissæ against the corresponding temperatures of the substance A as
ordinates, and a straight line drawn through the two points thus
obtained. From this straight line curve, now, different ratios can be
read off, and also the corresponding values of the absolute tempera-
tures of substance A. By dividing the absolute temperature T of
substance A by the corresponding value of the temperature ratio, the

* *Loc. cit.*

temperature T' is obtained, at which the solubility of B is equal to that of A at the temperature T. In this way the solubilities of B covering the range of known solubilities of A can be calculated.

I have tested this method in the case of a considerable number of substances of very varied character and solubility, and have, in all cases, found a very satisfactory agreement between the values of the solubility as calculated by means of the above method and those determined experimentally. This is readily apparent from Tables II, III, IV, and V.

In the following tables the solubilities are expressed in gramme-molecules of substance in 100 gramme-molecules of solvent (water). With regard to the solubilities of zinc chloride and bromide, and of cadmium bromide, the values obtained by R. Dietz* were employed. In the case of the other salts, the solubilities of potassium chloride and bromide were determined by de Coppet;† those of potassium nitrate by Andreä,‡ and those of the oxy-benzoic acids by Walker and Wood.§ The values of R, or the ratio T/T' are calculated by means of the temperatures marked with an asterisk.

Table II.—$ZnBr_2$ and $ZnCl_2 . H_2O$.

$c = 0 \cdot 00316$.

| Solubility observed. | Solubility of 2 calculated. | Abs. temp. for 1 observed. | Abs. temp. for 2 observed. | Abs. temp. for 2 calculated. | Ratio of temperatures. |
|---|---|---|---|---|---|
| 46·9 | 47·2 | 308·0 | 283·2 | 283·6 | 1·086 |
| 47·4 | — | 313·0* | 283·9* | — | 1·102 |
| 48·0 | 48·0 | 319·2 | 284·5 | 284·4 | 1·122 |
| 49·5 | 49·5 | 333·0 | 285·7 | 285·7 | 1·165 |
| 50·0 | — | 338·0* | 286·2* | — | 1·181 |
| 51·5 | 51·2 | 352·0 | 287·6 | 287·3 | 1·225 |
| 52·5 | 51·8 | 360·7 | 288·4 | 287·8 | 1·253 |
| 53·8 | 52·9 | 372·5 | 289·4 | 288·7 | 1·290 |

As can be seen from the above table, the solubility of the zinc bromide changes much less rapidly with the temperature than that of zinc chloride. Since the solubility curve of zinc chloride is rather steep, a comparatively small error in the temperature gives a comparatively large error in the calculated value of the solubility. The agreement, nevertheless, between the calculated and the determined values of the solubility is very satisfactory.

* 'Wissenschaftliche Abhandlungen der Physikalisch-technischen Reichsanstalt'; and 'Berichte D. Chem. G.,' 1899, vol. 32, p. 90.
† 'Ann. de Chimie' [5], vol. 30, p. 414.
‡ 'Jl. Prakt. Chem.,' vol. 137, p. 474.
§ 'Trans. Chem. Soc.,' 1898, vol. 73, p. 618.

Table III.—KBr and KCl.

$c = -0\cdot0001488.$

| | | | | | |
|---|---|---|---|---|---|
| 7·0 | 6·9 | 259·5 | 277·2 | 276·9 | 0·9370 |
| 8·0 | — | 272·6* | 291·5* | — | 0·9351 |
| 9·0 | 9·1 | 285·5 | 305·5 | 305·9 | 0·9331 |
| 10·0 | 10·0 | 297·8 | 319·7 | 319·7 | 0·9313 |
| 11·0 | 10·9 | 310·5 | 334·1 | 334·0 | 0·9294 |
| 12·0 | — | 323·0* | 348·2* | — | 0·9276 |
| 13·0 | 12·9 | 335·5 | 362·5 | 362·4 | 0·9257 |
| 14·0 | 13·85 | 347·7 | 377·1 | 376·2 | 0·9239 |

Table IV.—$CdBr_2 . 4H_2O$ and $KNO_3$.

$c = 0\cdot00148.$

| | | | | | |
|---|---|---|---|---|---|
| 4·2 | 4·0 | 274·0 | 289·5 | 288·6 | 0·9494 |
| 4·6 | — | 278·0* | 291·4* | — | 0·9553 |
| 5·8 | 6·0 | 288·0 | 296·0 | 296·8 | 0·9701 |
| 6·6 | 6·87 | 293·0 | 298·7 | 299·7 | 0·9775 |
| 7·6 | 7·8 | 298·0 | 302·0 | 302·5 | 0·9849 |
| 8·7 | — | 303·0* | 305·3* | — | 0·9924 |
| 10·0 | 9·61 | 308·0 | 309·3 | 308·0 | 0·9998 |
| 11·4 | 10·60 | 313·0 | 313·0 | 310·8 | 1·007 |

The very satisfactory agreement found in the case of the above salts is of interest from the fact that the two substances are ionised in a very different degree.

Table V.—*m*- and *p*-Oxybenzoïc Acids.

$c = 0\cdot00104.$

| | | | | | |
|---|---|---|---|---|---|
| 0·088 | 0·0868 | 286·8 | 300·0 | 300·7 | 0·9537 |
| 0·096 | 0·0976 | 288·7 | 301·7 | 302·1 | 0·9556 |
| 0·108 | — | 291·5* | 304·1* | — | 0·9586 |
| 0·116 | 0·114 | 293·2 | 305·6 | 305·3 | 0·9603 |
| 0·124 | 0·124 | 295·1 | 306·6 | 306·6 | 0·9623 |
| 0·136 | 0·1396 | 297·5 | 308·0 | 308·3 | 0·9648 |
| 0·148 | 0·1528 | 299·5 | 309·2 | 309·7 | 0·9669 |
| 0·172 | 0·1756 | 303·1 | 311·8 | 312·2 | 0·9706 |
| 0·190 | — | 305·0* | 313·6* | — | 0·9726 |
| 0·210 | 0·202 | 307·0 | 316·0 | 315·0 | 0·9746 |
| 0·220 | 0·206 | 307·9 | 317·1 | 315·6 | 0·9756 |
| 0·240 | 0·2156 | 309·8 | 318·9 | 316·9 | 0·9775 |

The preceding examples are only a few of the cases in which I have tested the validity of the relationship above stated, and, as can be seen, the agreement between theory and experiment is very satis-

factory. An equally good agreement was also shown in the other cases which I investigated. From the considerable number of cases I have studied, it would appear that the above method can be applied to the calculation of solubilities with close approximation to the truth. As to the range of temperatures or solubilities over which the relationship holds good, no definite statement can be made as yet. In almost all cases the relationship was tested over the whole range of available data ; that is to say, over the range of temperatures within which the two substances under comparison have equal solubilities. Several of the deviations are no doubt due to inaccuracies in the determination of the solubilities, and to errors in the drawing of the curves or reading from them.

II. *Calculation of Equilibrium Constants.*—The formula of Ramsay and Young, further, can be applied not only, as has already been shown, to the calculation of vapour pressures and of solubilities, but it can also be used for the purpose of calculating the equilibrium constants of chemical reactions. In this case, R and R′ denote the ratios of the absolute temperatures at which the values of the equilibrium constant of the two reactions are equal. In this case, also, if we know the temperature curve of the equilibrium constant of one reaction, it will be possible to calculate the temperature curve of the equilibrium constant of another reaction, by determining the value of that constant at two temperatures. This is shown by the figures given in Table VI. The two reactions which were compared were those represented by the equations $2HI \rightleftharpoons H_2 + I_2$,* and $2CH_3 . CO . CH_3 \rightleftharpoons CH_3 . CO . CH_2 . C (CH_3)_2OH$,† two reactions, therefore, which are of a most dissimilar character. As the values of the equilibrium constant of these two reactions were not determined at a sufficient number of suitable temperatures for the present purpose, it was necessary to calculate the values of the constant at other temperatures. In the case of hydriodic acid, the constant was calculated for the temperatures 520°, 530°, 540°, 550°, 560°, by means of the formula given by Bodenstein :‡

$$\log_e K = \frac{90 \cdot 48}{T} - 1 \cdot 5959 \log_e T + 0 \cdot 0055454\,T + 2 \cdot 6981.$$

The values found were :—

| $t$ ......... | 520° | 530° | 540° | 550° | 560° |
|---|---|---|---|---|---|
| K......... | 0·02563 | 0·02658 | 0·02759 | 0·02864 | 0·02974 |

In the case of the condensation of acetone to diacetone alcohol, in which case the equilibrium constant was determined at only two

* Bodenstein, ' Zeitschr. Physik. Chem.,' 1899, vol. 29, p. 295.
† Koelichen, ' Zeitschr. Physik. Chem.,' 1900, vol. 33, p. 129.
‡ *Loc. cit.*

temperatures, viz., 0° and 25·2°, the values of the constant were calculated at 10°, 40°, 60°, 80°, 100°, by means of the integrated form of the van't Hoff equation :

$$\log_e K_1 - \log_e K_2 = \frac{q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

the value of $q$, the heat of reaction, being regarded as constant and equal to $-$ 77·4 centuple calories :[*] R is the " gas constant." The error introduced here can scarcely be very large.

Table VI.

| Equilibrium constant. | Equilib. constant for 2, calc. | Absol. temp. for 1 observed. | Absol. temp. for 2 observed. | Absol. temp. for 2 calc. $c = 0\cdot0114$. | Rat·o of temperatures. |
|---|---|---|---|---|---|
| 0 ·0266 | 0 ·0265 | 805°·2 | 379°·0 | 380°·4 | 2 ·1162 |
| 0 ·0270 | — | 809 ·5* | 374 ·0* | — | 2 ·1644 |
| 0 ·0275 | 0 ·0275 | 814 ·0 | 368 ·0 | 367 ·5 | 2 ·2148 |
| 0 ·0280 | — | 818 ·0* | 362 ·0* | — | 2 ·2596 |
| 0 ·0285 | 0 ·0283 | 821 ·5 | 356 ·0 | 357 ·3 | 2 ·2988 |
| 0 ·0290 | 0 ·0285 | 826 ·0 | 350 ·0 | 351 ·6 | 2 ·3492 |
| 0 ·0295 | 0  0292 | 829 ·0 | 344 ·0 | 347 ·9 | 2 ·3828 |

As can be seen from the above figures, the agreement between the calculated and determined values of the equilibrium constants is exceedingly good, especially when one considers how different the two reactions are in character and also that in one case the equilibrium constant increases, in the other case, diminishes with the temperature.

So far, this is the only case in which I have been able to test the application of the formula R $=$ R' $+ c$ ($t' - t$) to the calculation of equilibrium constants. On account, however, of the analogy existing between the change of the vapour pressure, solubility, and equilibrium constant, with the temperature, it may be confidently expected that when other cases come to be tried, confirmation of the relationship will be obtained.

On account of the practical importance of the above relationships, I have thought it well, in this preliminary note, to publish them in the present empirical form. I hope, however, at a later time, to discuss the question in greater detail, with the help of a larger number of examples, and also to examine the subject from the theoretical stand-point. It may, however, be remarked here, that the whole work has been based on the form of the thermodynamic equation given by van't Hoff, $\dfrac{d\log_e x}{dt} = \dfrac{Q}{RT^2}$, an equation which at once shows the

* Koelichen, *loc. cit.*

analogies existing between vapour pressures, solubilities, and equilibrium constants of chemical reactions.

III. *Empirical Formula for Latent Heats of Vaporisation.*—During the progress of the preceding work, I was led by a consideration of certain empirical formulæ put forward a number of years ago by W. C. Unwin,[*] connecting the pressure, temperature, and volume of saturated vapours, to a formula by means of which from the latent heats of vaporisation of one substance the values of the latent heats of vaporisation of another substance may be calculated. If $L_1$ is the known latent heat at the absolute temperature $T_1$ of the first substance, and $L_2$ the latent heat of the second substance at the temperature, $T_2$, at which the vapour pressure of the second substance is equal to that of the first substance at the temperature $T_1$, then $L_1 = L_2 \, T_2{}^x$, where $x$ is a constant. A formula which is derived with greater strictness, but which contains two constants, is $L_1/L_2 = T_1{}^{x1}/T_2{}^{x2}$. In some cases the latter formula gives somewhat better values than the former, but for most purposes the simpler formula may be employed. These formulæ appear to be suitable for calculating the latent heats of vaporisation at not too high pressures, but break down in some cases at pressures over 10,000 mm., although in other cases they hold even at pressures of over 20,000 mm.

In Tables VII and VIII are contained some of the results which have been obtained using the simpler formula.

Table VII.—Benzene and Methyl Acetate. $x = -0.008847$.

| Pressure in mm. | Absol. temp. of benzene. | Absol. temp. of methyl acetate. | Heat of vaporisation of benzene. | Heat of vaporisation of methyl acetate. | |
|---|---|---|---|---|---|
| | | | | Deterd. | Calc. |
| | ° | ° | cal. | cal. | cal. |
| 1335 | 373 | 347·3 | 92·06 | 96·95 | — |
| 4335 | 423 | 390·9 | 81·01 | 83·51 | 85·40 |
| 10650 | 473 | 433·4 | 69·14 | 70·95 | 72·95 |
| 22182 | 523 | 475·0 | 49·71 | 52·28 | 52·49 |

As can be seen, the agreement between the determined and calculated values of the latent heat of vaporisation, is very good. In some cases, however, which I have investigated, *e.g.*, in the case of benzene and hexane, the agreement is not quite so good.

The values of the latent heats of vaporisation of benzene, methyl acetate, and ethyl alcohol, given in the fourth and fifth columns of the

[*] 'Phil. Mag.,' 1886, vol. 21, p. 299.

Table VIII.—Benzene.and Ethyl Alcohol.   $x = -0.1297$.

| Pressure in mm. | Absol. temp. of benzene. | Absol. temp. of ethyl alcohol. | Heat of vaporisation of benzene. | Heat of vaporisation of ethyl alcohol. | |
|---|---|---|---|---|---|
| | | | | Deterd. | Calc. |
| | $\overset{\circ}{}$ | $\overset{\circ}{}$ | cal. | cal. | cal. |
| 26·54 | 273 | 285·0 | 106·17 | 221·0 | — |
| 268·3 | 323 | 327·4 | 99·72 | 214·96 | 211·3 |
| 1335 | 373 | 366·4 | 92·06 | 200·2 | 198·0 |
| 4335 | 423 | 403·3 | 81·01 | 177·5 | 176·4 |
| 10650 | 473 | 438·5 | 69·14 | 152·7 | 152·2 |
| 22182 | 523 | 473·2 | 49·71 | 116·6 | 110·5 |

Tables VII and VIII, were calculated by means of the thermodynamic equation

$$\frac{L}{s_1 - s} = \frac{T}{J} \cdot \frac{dp}{dt},$$

using the data of Ramsay and Young[*] for ethyl alcohol ; of Young[†] for benzene ; and Young and Thomas[‡] for methyl acetate.

It is probable that, in some cases at least, a formula similar to that given above may be used for the calculation of heats of solution and of chemical reaction, but at present the data necessary for testing this are not available.

*Summary.*

1. It is shown that by means of the equation $R = R' + c\,(t' - t)$ (*vide* p. 471), vapour pressures (Ramsay and Young), solubilities, and the equilibrum constants of chemical reactions can be calculated.

2. The latent heat of vaporisation of a substance can be calculated from the latent heat of vaporisation of another substance, within a certain range, by means of the empirical equation $L_1 = L_2\,T_2{}^x$.

[*] 'Phil. Trans.,' 1886, Part I, p. 71.
[†] 'Trans. Chem. Soc.,' 1891, vol. 59, p. 134.
[‡] *Ibid.*, 1893, vol. 63, p. 1210.